Project Note

Date:	March 26, 2008	**Project No.:**	TTEMI-05-003-0019
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Subject:	Rationales for Data Qualifiers		

PROJECT NOTE SUMMARY

In contacted Mr. Charlie Appleby of the U.S. Environmental Protection Agency, Region 4 Science and Ecosystem Support Division (SESD), Management and Technical Services Branch (MTSB), Quality Assurance Section to obtain assistance with rationales for data qualifiers in the data qualifier reports for EPA Contract Laboratory Program (CLP) analytical data packages and rationales for data qualifiers in SESD Analytical Support Branch (Regional Laboratory) analytical data packages.

Data qualifiers in CLP and SESD ASB analytical data packages were provided to Mr. Appleby and Mr. Appleby provided input on the bias direction (high, low, or unknown) for J-flagged (estimated) data. Also, Mr. Appleby provided information regarding revisions in terms used in the CLP and SESD ASB analytical data packages. For example, the term minimum quantitation limit has been replaced with minimum reporting limit.

RESPONSE REQUIRED

(x) None ( ) Phone call ( ) Memo ( ) Letter ( ) Report

Below is a list of reasons for estimated data gathered from numerous CLP data packages. The determinations of the biases provided were obtained from Denise Goddard and Diane Guthrie. Please let me know if the bias determinations for the reason for estimated data are still accurate based on new procedures in the Quality Assurance Branch.

- **Less than quantitation limit** - When the concentration reported in the sample is less than the quantitation limit, the bias is unknown; a high or low bias cannot be determined. Still valid

- **Holding times exceeded** - When a sample was analyzed after the required holding time, the concentration reported is biased low. The substance is present in the sample; however, possibly at a lower concentration than if the sample was analyzed within the required holding time. This is valid for most analytes. However, certain polychlorinated organics may dechlorinated to form other target analytes. For example, tetrachloroethene may dechlorinated into tri- or di-chloroethene or even vinyl chloride. The same may take place with PCBs. In these situations, the bias would probably be low for the more chlorinated analytes, but may be high for the less chlorinated analytes.

- **Low surrogate recovery** - If the surrogate recovery is low, the bias is also low. Still valid

- **Erratic MS/MSD recovery due to sample non-homogeneity** -A bias cannot be associated in this case. The variations in particle size affect the homogeneity of the sample. Still valid

- **Blind spike recovery >or <the warning limit** - If the blind spike recovery is greater than the warning limit, the bias is high. If the blind spike recovery is less than the warning limit, the bias is low. This is the same for the action limit. These samples are spiked to determine the laboratory's accuracy of analysis. Still valid

- **Serial dilution percent Difference = % (a specific percent is usually provided)** - The serial dilution percent difference refers to accuracy in sample analyses. The serial dilution percent difference should be ±10 percent of the standard. In cases where the percent difference is greater than ±10 percent of the standard, a bias cannot be associated with the concentration reported as estimated.

  The serial dilution result is really compared to the undiluted sample. This is why there are criteria for the initial result (at least a factor of 50 above the IDL). If the difference is greater than 10%, then there is a bias associated with measuring the analyte in the presence of other matrix components. The direction of this bias would be unknown.

- **Only analysis of 2 times the contract-required detection limit (CRDL) standard required by contract statement of work (SOW) for inductively coupled plasma (ICP) analysis** - A bias is not associated with this rationale. Still valid

- **Suspected over correction as noted in the contractor Inter-elemental Correction Sample (ICS)** -The Bias is low in this case. This statement also indicates that the sample was analyzed by a Contract Laboratory Program (CLP) laboratory. Still valid, although non-CLP labs also use the CLP methods.

- **Matrix spike recovery percent less than 100 percent** - The spike recovery should equal 100 percent. A recovery below 100 percent will usually be low bias. The recovery should be compared to the actual recovery limits posted in the current SOW. Also, if there is a positive concentration of the spiked analyte in the unspiked sample, the bias may be unknown (and if that level is > 4 x amount spiked, the reviewers disregard the recovery).

- **Matrix spike recovery percent greater than 100 percent** - The spike recovery should equal 100 percent. A recovery greater than 100 percent will usually be a high bias. See note above.

- **Matrix duplicate relative percent difference (RPD) (a percent is usually given)** - The matrix duplicate RPD deals with precision in sample analysis. The RPD should be ±10 percent of the standard. When the RPD is outside of the range, the precision in sample analysis is questionable. Also, a bias cannot be associated with this rationale. Still valid

- **Missed from PE sample, but present in the environmental sample** - If a substance was not detected in the performance evaluation (PE) sample, and is present in the environmental samples for the data set, the bias is low. The PE sample is also referred to as the standard. Also, if a substance is not detected in the standard or PE sample, it is possible that the substance is present in environmental samples in the data set where the concentration for that specific substance was reported as not detected. If this situation occurs, non-detect results will carry an "R" flag and should not be used. If positive, it would have a low bias, the magnitude of which is not known.

Please provide assistance with determining the bias (high, low, unknown, or none) of the following reasons for estimated data. These were obtained from CLP analytical data packages.

- Erratic continuing calibration – Would need to know the direction of the bias. Then, generally that will tell the direction of your bias.
- High surrogate recovery - high bias
- Poor instrument response - low bias
- Calibration outliers - As above, need to know direction of outlying results, above expected values or below (equals high bias or low, respectively).

Below is a list of other issues that often come up when reviewing analytical data packages for inclusion in hazard ranking system (HRS) documentation records.

- Biases are not associated with serial precision. Serial precision deals with accuracy in analysis. It indicates the ability to consistently determine the concentration of an analyte, even if a dilution was done. Possibly. Not sure I understand this one.

- If there is a high precision error, a different analysis technique may be necessary. Usually, an analysis technique is chosen to analyze for a whole range of parameters. However, if there is a contaminant of concern, a specific analysis technique that is expected to provide the most accurate sample results can be chosen. If the same sample cannot be reanalyzed, then re-sampling may be necessary. Possibly. Not sure I understand this one either.

- When referring to a bias in a sample, the bias is not specific to the sample. Quality control (QC) samples are done for a batch of samples. The sample that is actually analyzed as the quality control (QC) sample is the standard; and the bias is specific to the standard. Therefore, for the environmental samples for the project, the bias is actually a "predicted bias," which is based on the standard. In order to determine a specific bias for each environmental sample, a QC analysis would have to be performed for each environmental sample analyzed, and that is not feasible.

  Actually, when we do a matrix spike, that is specific to the sample which was spiked, although inferences may be made as to the bias in samples of a related matrix type. Generally, for organics we do not make such inferences during our review, but we do for inorganics. Also for organics or for ICP-MS, we can consider surrogate standard recovery to be sample-specific.

- Confirmed by Gas chromatography/Mass Spectrometry (GC/MS) means that a definite identification of the analyte has been determined. The GC Detector indicated that there is a definite hit for that analyte. Rather than "definite", I would say "nominal". This means that with the combination of retention time mass spectral matching (typically at unit mass resolution), there is a high likelihood of a match, but it is not definite.

- A Method Detection Limit (MDL) is not a real number. An MDL is set for the instrument and a method. The MDL is usually multiplied by 3, 5, or 10 depending on the analyte. A flag is assigned and the data is reported as estimated if the concentration of the analyte is below the minimum quantitation limit (MQL). In such cases, the concentration of the analyte is usually between the MQL and the MDL. The MDL is typically multiplied by a factor to estimate where to set the *method quantitation limit* or MQL. These days, we usually require the lab to run a standard at or near their MQL that must pass both qualitative and quantitative criteria.

- *The concentration of the matrix spike is known. The percent recovered should be between two numbers, 75 to 125 percent. If, the percent recovered is below 75 percent, the bias is low. If the percent recovered is above 125 percent, the bias is high. This explanation is different from the ones listed above, which deal with recoveries that are < or > 100 percent.* Before drawing conclusions from recovery, it is better to have laboratory-derived limits. In the case of CLP data, the limits posted in the SOW have been derived from studies involving several labs.

Based on our conversation on September 4, 2007, if a data package indicates that a sample concentration is less than the CRQL, MQL, or MRL, that means that the analyte was not detected above the reporting limit or the lowest demonstrated level of acceptable quantitation. True